



## The control of selectivity in gas-phase glycerol dehydration to acrolein catalysed by sulfated zirconia

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### ABSTRACT

This paper is about the synthesis of acrolein by means of glycerol dehydration in the gas phase, catalysed by sulfated zirconia. The reaction parameters affecting glycerol conversion and selectivity to acrolein, the contribution of homogeneous reactions and roles of co-fed oxygen and of diffusion constraints were examined, in relation to the complex reaction network. The best selectivity to acrolein, 42% obtained at 49% glycerol conversion, was achieved by combining conditions that limit the occurrence of consecutive reactions from acrolein, leading to acetaldehyde and to heavy compounds, whilst minimizing mass-transfer inter-particle limitations. These findings are of general interest in relation to both the transformation of glycerol into acrolein by means of gas-phase dehydration, and the use of sulfated zirconia catalysts for high-temperature acid-catalysed reactions.

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### 1. Introduction

Glycerol will play a crucial role in future bio-refineries, because its derivatives can be used in various sectors, such as the fuels, chemicals, pharmaceuticals, detergents, and building industries [1–3]. In this context, the catalytic dehydration of glycerol to acrolein has attracted great interest in recent years [4–17]; acrolein is mostly used as an intermediate for the synthesis of acrylic acid, this reaction being catalysed in current industrial processes by Mo/V/W mixed oxides [18]. Several catalysts with Brønsted-type acid properties have been reported to achieve excellent performance in glycerol dehydration, yielding total glycerol conversion and selectivity to acrolein of 70–90%, as shown in the recent review by Katryniok et al. [4]. The best-performing catalysts are WO<sub>3</sub>/ZrO<sub>2</sub> [5,6], supported Keggin polyoxometalates [7–9], V/P/O [10,13], rare earth pyrophosphates [11], and H-ZSM5 [12,14].

In general, strong acidity is required in order to facilitate the double intra-molecular dehydration of the reactant, although strong acidity may also be responsible for the formation of heavy compounds; the latter also contribute to the catalyst deactivation, since they accumulate on the catalyst surface [15]. Other impor-

tant factors include textural properties, such as the porosity of the support, because if steric limitations do not allow the rapid counter-diffusion of the products, the formation of heavy compounds by bimolecular condensation and of coke may lead to catalyst deactivation [16].

One further characteristic of this reaction is that with many of the strongly acidic catalysts investigated in papers, the co-feed of oxygen helps to keep the catalytic surface cleaner while limiting the formation of heavy deposits that may lead to catalyst deactivation [4,19]. The co-feed of oxygen during gas-phase acid-catalysed reactions is not an usual feature of these reactions, because the addition of oxygen impurities can enhance the formation of high-boiling, oxygenated compounds, which make deactivation even quicker than without oxygen, unless a metal promoter is added to facilitate the *in situ* combustion of residues [20].

Among the various systems investigated in the literature, little attention has been given to sulfated zirconia [5,15]. We decided to investigate the catalytic behaviour of sulfated zirconia, although this system is reported to afford only moderate selectivity to acrolein, in order to understand how the interplay of acidity and reaction parameters affect selectivity to the desired product. Moreover, sulfated zirconia might, in principle, be the most suitable catalyst for this reaction in the presence of molecular oxygen, since it combines both acid and redox properties [21–25]; the latter may help in accelerating the removal of heavy compounds incipiently formed on the catalyst surface.

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## 2. Experimental

The catalyst was prepared via a conventional precipitation method [26].  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  (99%, FLUKA) was dissolved in distilled water and added with a peristaltic pump under vigorous stirring to an ammonia solution (30%, AnalaR). During the entire course of the precipitation, the pH value was kept constant at  $10.0 \pm 0.1$  by the continuous addition of a 5N ammonia solution. After the complete addition of the salt solution, the hydroxide suspension was aged for 20 h at  $90^\circ\text{C}$  under reflux conditions. The aged hydroxide was filtered and washed with warm distilled water until it was free from chloride ions ( $\text{AgNO}_3$  test). The Zr hydroxide was dried at  $110^\circ\text{C}$  and then impregnated with  $(\text{NH}_4)_2\text{SO}_4$  by an incipient wetness method. The sample was finally calcined at  $650^\circ\text{C}$  for 3 h in flowing air. The final content of S in catalyst was the 4.4 wt% (expressed as sulfate); the surface area was  $122 \text{ m}^2/\text{g}$  ( $80 \text{ m}^2/\text{g}$  for the untreated  $\text{ZrO}_2$ ).

Catalyst surface acidity was measured by means of FT-IR spectroscopy in transmittance mode, using a Perkin-Elmer 1750 Spectrometer. Self-supporting wafers of sample were first evacuated at  $450^\circ\text{C}$  (residual  $P = 10^{-6}$  mbar). Then, the adsorption of pyridine was carried out at room temperature, and desorption was carried out by out-gassing the sample at increasing temperatures. The FT-IR spectrum was recorded after evacuation at each temperature level. The concentration of Lewis and Brønsted acid sites was calculated using the method proposed by Eines (extinction coefficient for Lewis sites 2.22, for Brønsted sites 1.67) [27].

Thermal-Programmed-Desorption (TPD) measurements were carried out using a Thermoquest TPDRO1100 instrument. 0.1 g of the sample was loaded in a quartz reactor, and pretreated in a He flow at  $100^\circ\text{C}$  before the temperature-programmed heating. The temperature was linearly increased up to  $650^\circ\text{C}$  (thermal ramp:  $10^\circ\text{C}/\text{min}$ ). The outlet flow was analyzed by means of a TCD and an on-line VGQ Mass Spectrometer equipped with a quadrupole analyzer.

Catalytic tests of glycerol dehydration were carried out using a continuous flow reactor made of glass (internal diameter 11 mm, catalyst particles diameter 0.25–0.60 mm), operating at atmospheric pressure. An axial thermocouple allowed us to measure the temperature inside the catalytic bed. 0.1 g of catalyst was loaded in the form of granules, with a diameter ranging from 0.25 to 0.60 mm; granules were prepared by grinding pellets, which had been prepared by pressing the catalyst powder. Overall reactor gas residence time was 0.2 s (unless otherwise specified), which corresponds to a GHSV value of  $18,000 \text{ h}^{-1}$ , and  $360 \text{ h}^{-1}$  if referring to glycerol only. Tests at high linear velocity were carried out by increasing the inlet gas velocity; the catalyst amount was also varied, in order to obtain the desired GHSV value. Two different feed compositions were used: (i) an anaerobic feed, containing 2 mol% glycerol, 40 mol% water and 58 mol% helium; (ii) an aerobic feed, containing 2 mol% glycerol, 4 mol% oxygen, 40 mol% water and 54 mol% helium.

The effluent stream was bubbled through two in-series abatement devices, which were filled with water (but in some cases anhydrous acetone was used, for the identification of compounds which are less soluble in water) and maintained at a temperature of  $0\text{--}2^\circ\text{C}$ ; a third refrigerated condenser was not filled with any solvent. Several preliminary experiments were carried out in order to determine whether the abatement system was an efficient way to solubilise and condensate all the reaction products, except carbon oxides; special care was taken to optimise the system in order to have a complete abatement of the very volatile acrolein. After this abatement, the gaseous stream, still containing oxygen and carbon oxides, was fed to an automatic sampling system for gas-chromatography (GC) analysis. The water solution containing the unconverted glycerol and reaction products was analyzed by GC, using a Hewlett-Packard 5890 instrument equipped with a TCD detector. A semi-capillary wide-bore OV 351 (polyethylen-

glycol treated with terephthalic acid) column was used for the separation of condensed compounds; oven temperature was programmed from  $40^\circ\text{C}$  to  $190^\circ\text{C}$  (heating rate  $10^\circ/\text{min}$ , isothermal step at  $190^\circ\text{C}$ , 3 min), then from  $190^\circ\text{C}$  to  $225^\circ\text{C}$  (heating rate  $30^\circ/\text{min}$ , final isothermal step at  $225^\circ\text{C}$ , 25 min). Two wide-bore columns were used for the separation of non-condensable products: a Molsieve 5A for oxygen and CO, and a Silica Plot for  $\text{CO}_2$  (oven temperature,  $80^\circ\text{C}$ ).

A few unknown compounds were eluted in the GC column; we attributed to these compounds the same response factor of the known compound with the closer retention time. In the figures, minor identified products and unknown compounds were included together under the heading "Others". Compounds were identified by means of GC-MS, and by the injection of pure reference standards for the comparison of retention times in the GC column.

## 3. Results and discussion

### 3.1. Surface acidity of zirconia and sulfated zirconia

Sulfated zirconia catalysts are classified as strongly acid catalysts [28,29], but water is reported to be needed for high catalytic activity, since it facilitates the generation of "superacidic" Brønsted sites, and even it may be necessary to retain surface hydroxylation at high temperature [30,31]. Even when used for glycerol dehydration, sulfated zirconia is claimed to belong to the class of very strong acid catalysts [15].

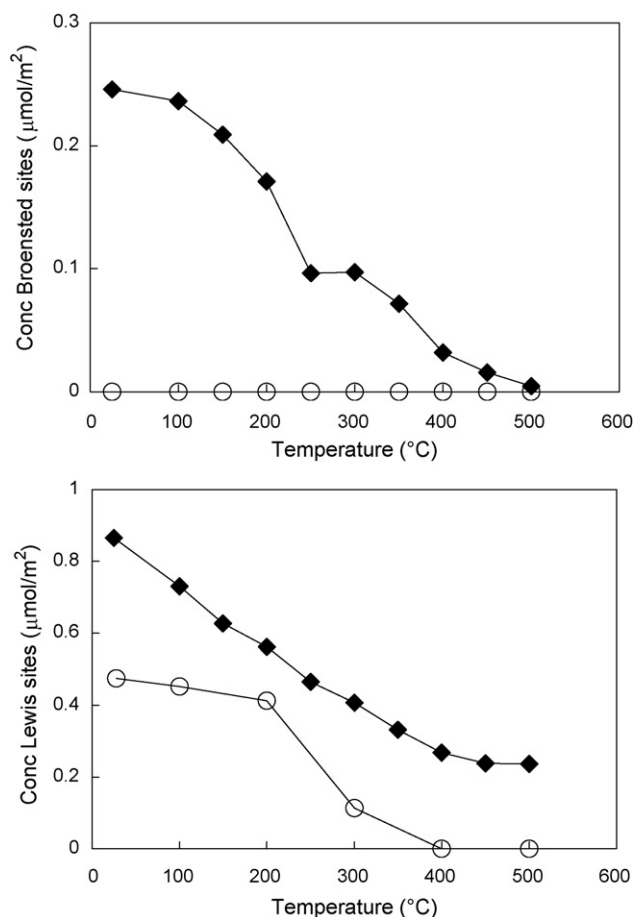
Fig. 1 shows the changes in the concentration of pyridine adsorbed on surface Brønsted and Lewis sites in zirconia and in sulfated zirconia, in function of the desorption temperature, after adsorption at room temperature. The main results were as follows:

1. As expected, non-sulfated zirconia showed no Brønsted acid sites at all. The concentration of pyridine adsorbed on Brønsted sites in the sulfated zirconia sample decreased when desorption temperature increased, but still remained non-negligible even at a high temperature.
2. The strength of Lewis sites was greater in the sulfated zirconia than in the untreated zirconia; some residual adsorbed pyridine was left even after treatment at  $500^\circ\text{C}$ . This indicates that the presence of sulfate enhances the Lewis acidity of  $\text{Zr}^{4+}$  [32]. The concentration of Lewis sites was higher than that of Brønsted sites; therefore, it may be expected that during reaction, in the presence of water, the Zr–OH groups generated by water adsorption over strong Lewis sites can play a role in glycerol dehydration.

In fact, Fig. 2, plotting the intensity of the signal of  $\text{H}_2\text{O}$  released from the sulfated zirconia catalyst recorded while heating the sample in an He flow, from room temperature up to  $500^\circ\text{C}$  (TPD experiment), shows that water was completely released from the sample only at around  $420\text{--}440^\circ\text{C}$ , that is higher than the maximum temperature used for reactivity experiments. Peaks can be associated to the loss of water interacting with either Lewis  $\text{Zr}^{4+}$  sites or S–OH moieties, and to the dehydrative condensation of sulfuric groups into pyrosulfate [33].

### 3.2. Reactivity tests: blank experiments

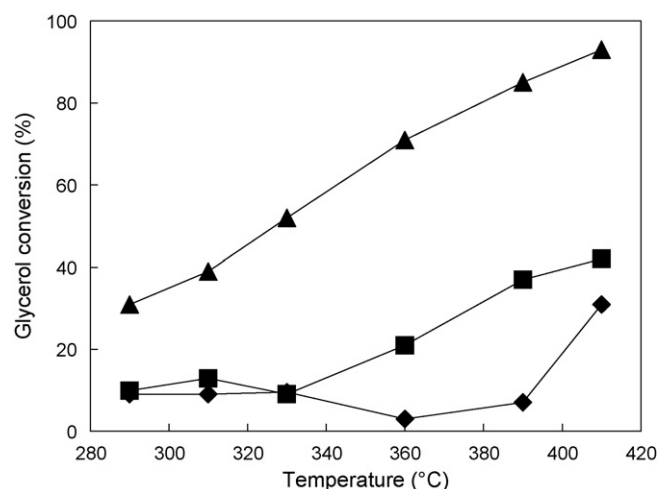
Preliminary experiments were carried out in function of temperature but without any catalyst in the empty reactor (without any inert filling material), in order to assess the contribution of thermal homogeneous reactions to glycerol conversion. The results of these experiments are shown in Fig. 3 for tests carried out both in the absence and presence of co-fed oxygen. In the  $290\text{--}390^\circ\text{C}$  temper-



**Fig. 1.** Concentration of Brønsted sites (top) and Lewis sites (bottom) in zirconia and sulfated zirconia catalysts in function of the temperature of treatment after the adsorption of pyridine at room temperature. Samples were pretreated at 450 °C under vacuum before the adsorption of pyridine. Symbols: zirconia (○), and sulfated zirconia (◆).

ature range, glycerol conversion was below 10%. On the other hand, when 4% oxygen was added to the stream, the conversion became non-negligible at above 330 °C.

The main products found under these conditions were acrolein, acetaldehyde, hydroxyacetone, acetone, allylic alcohol, ethanol and propionaldehyde, and – in the presence of oxygen – also CO<sub>2</sub> (the



**Fig. 3.** Effect of temperature on glycerol conversion either without catalyst or with non-sulfated zirconia catalyst. Symbols: no catalyst, no O<sub>2</sub> in feed (◆); no catalyst, O<sub>2</sub> in feed (■), and ZrO<sub>2</sub> catalyst, O<sub>2</sub> in feed (▲). Feed composition (without O<sub>2</sub>): glycerol/water/helium = 2/40/58 (molar ratios). Feed composition (with O<sub>2</sub>): glycerol/oxygen/water/helium = 2/4/40/54 (molar ratios).

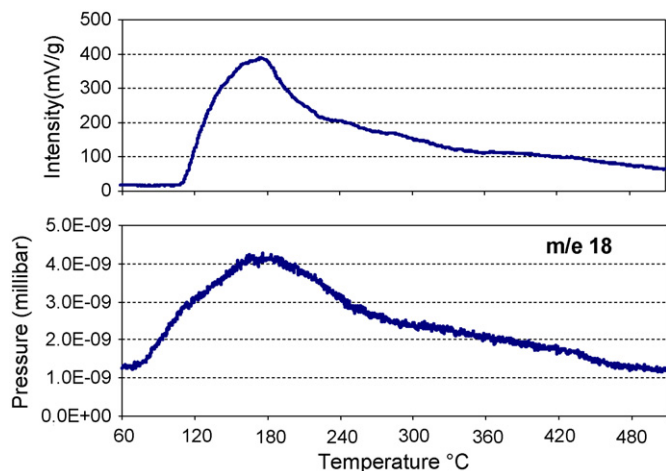
predominant product at above 360 °C) and acetic acid. The formation of heavy compounds (quantitatively evaluated as missing C in mass balance), in both the presence and absence of oxygen, was very likely; but could not be ascertained because – due to the very low conversion achieved – the C balance could not be properly evaluated.

The same figure also shows the conversion obtained with non-sulfated zirconia (tests in the presence of oxygen). Despite the absence of any Brønsted acidity, the catalyst produced a significant conversion of glycerol, but with very low selectivity to acrolein; the latter was less than 5% at a low temperature; but when the temperature was raised, it increased up to a maximum of 8–10% due to the contribution of homogeneous reactions. Several by-products formed – the same as those observed in the absence of catalysts – with yields that were also similar to those obtained with no catalyst at all. In fact, almost all the converted glycerol was transformed into heavy compounds.

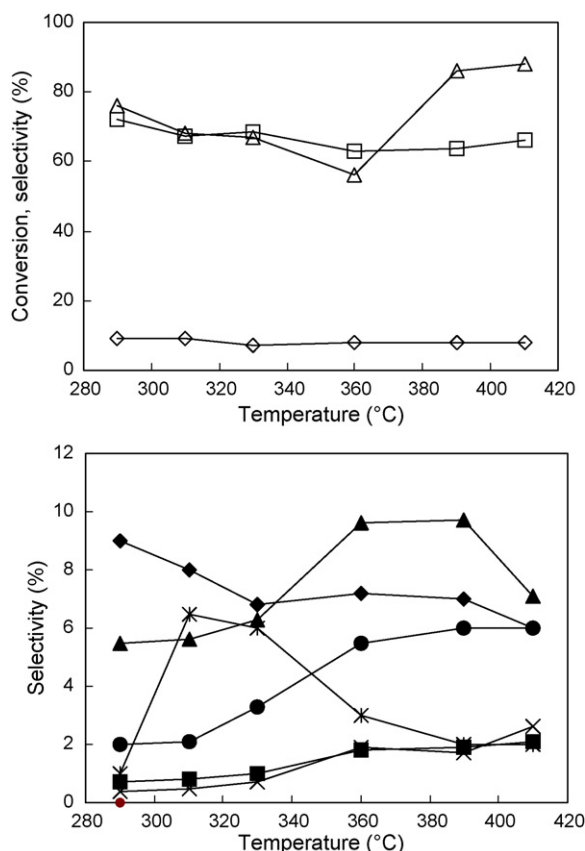
### 3.3. The reactivity of sulfated zirconia: anaerobic tests

Fig. 4 shows the results of experiments carried out without O<sub>2</sub> in feed, and with the sulfated zirconia catalyst. Fig. 4(top) plots the conversion of glycerol, the selectivity to acrolein and to heavy compounds; Fig. 4(bottom) plots the detail of main by-products: acetaldehyde, propionaldehyde, hydroxyacetone, acetone, and carbon monoxide. Some minor additional by-products, such as allyl alcohol and ethanol, have been grouped into “Others”; the latter also includes two unidentified compounds.

Glycerol conversion was close to 80% at 290 °C, but then decreased to 55% when the temperature was raised to 360 °C, possibly due to a deactivation phenomenon that counteracted the expected conversion increase. At higher temperatures, the significant conversion increase registered was likely due to the contribution of homogeneous reactions (see Fig. 3). The major products found were: acrolein (but with a selectivity lower than 10%), acetone, propionaldehyde, acetaldehyde, and CO – the latter probably formed by the reforming of organic compounds or aldehydes decarbonylation. However, the very low C balance suggests the relevant formation of heavy compounds (selectivity between 60% and 80%); these compounds were possibly responsible for the deactivation phenomenon observed.

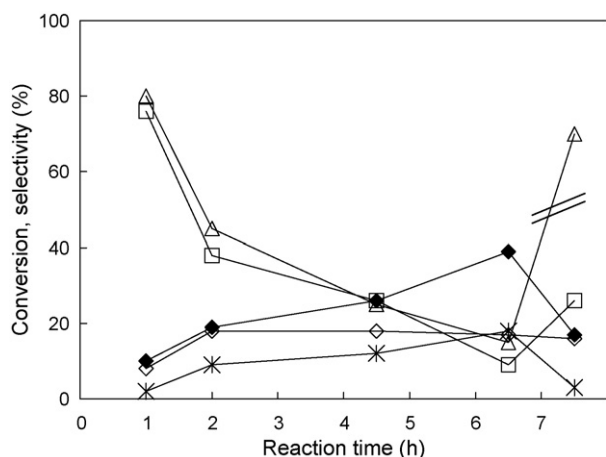


**Fig. 2.** TCD signal (top) and m/e = 18 quadrupole signal (H<sub>2</sub>O) (bottom) during thermal-programmed-desorption of water from sulfated zirconia catalyst.



**Fig. 4.** Effect of temperature on catalytic behaviour of sulfated zirconia catalyst in glycerol dehydration. Feed composition: glycerol/water/helium = 2/40/58 (molar ratios). Residence time 0.2 s; catalyst mass 0.1 g; linear velocity 0.15 m/min. Symbols: conversion of glycerol ( $\Delta$ ), selectivity to acrolein ( $\diamond$ ), heavy compounds ( $\square$ ), acetone ( $\blacklozenge$ ), acetaldehyde ( $\bullet$ ), propionaldehyde ( $\blacksquare$ ), CO ( $\times$ ), hydroxyacetone ( $*$ ) and others (minor identified + unknown compounds) ( $\blacktriangle$ ).

The presence of a deactivation phenomenon was confirmed by tests carried out under isothermal conditions at 310 °C, during increasing elapsed reaction times; Fig. 5 shows the results of this experiment (we reported only the selectivity of products that underwent top variations in time). The deactivation rapidly led to



**Fig. 5.** Effect of the reaction time on catalytic behaviour of sulfated zirconia catalyst in glycerol dehydration. Feed composition: glycerol/water/helium = 2/40/58 (molar ratios). Temperature 310 °C; residence time 0.2 s; catalyst mass 0.1 g; linear velocity 0.15 m/min. Symbols: conversion of glycerol ( $\Delta$ ), selectivity to acrolein ( $\diamond$ ), heavy compounds ( $\square$ ), acetone ( $\blacklozenge$ ) and hydroxyacetone ( $*$ ). The last point was taken after a regeneration of the catalyst in airflow for 3 h at 450 °C.

the decrease of glycerol conversion within a few hours of the reaction time. This also had important consequences on selectivity to products; in fact, the selectivity to heavy compounds – which was very high on the fresh catalyst – rapidly decreased, and after 7 h was about 10%. The selectivity to some products correspondingly increased; the greatest variation was observed with hydroxyacetone and acetone. Acetone – the prevailing product after a few hours reaction time – is reported to be formed by consecutive transformations of hydroxyacetone [13,14]. In our case, however, there was no relationship between the two compounds, since the selectivity to both acetone and hydroxyacetone increased. The selectivity to acrolein initially increased, but then remained constant at approximately 18–19%.

The fall of selectivity to heavy compounds observed in parallel with the decrease of conversion may be attributed to one of two different factors: (a) a decrease of conversion led to a lower contribution of consecutive reactions, meaning that heavy compounds mainly formed by condensation reactions on products such as acrolein itself; or (b) the accumulation of coke caused the deactivation of selected sites, which are responsible for the formation of heavy compounds.

The deactivated catalyst was treated in flowing air for 3 h at 450 °C, and then the catalytic behaviour was registered again (last point in Fig. 5). The initial activity of the fresh catalyst did not appear to have completely recovered after the regeneration treatment; in fact, the initial conversion was 70% (80% for the fresh catalyst).

### 3.4. The reactivity of sulfated zirconia: aerobic tests

Fig. 6 compares the catalytic behaviour in the absence and in the presence of O<sub>2</sub>. The positive effect of the addition of oxygen on performance is evident: the conversion of glycerol in the temperature range of 290–360 °C had declined in the absence of oxygen, but showed a continuous, albeit slight, increase when the temperature was raised in the presence of oxygen. On the other hand, in the latter series of experiments, the conversion increase was only of 8–9 point % over the entire temperature range, thus suggesting either the possible presence of mass-transfer inter-particle limitations under the conditions used, or the contribution of residual deactivation phenomena. Oxygen conversion was close to 70% at 410 °C.

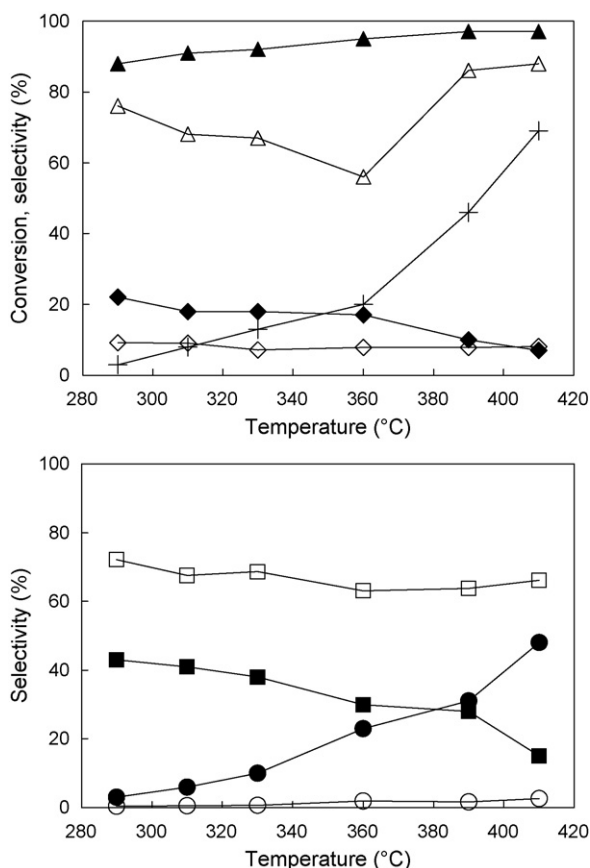
The selectivity to acrolein was slightly higher in the presence of oxygen, but the main effect was on the amount of heavy compounds, which considerably decreased; at the same time, the formation of CO and CO<sub>2</sub> became significant. However, deactivation phenomena were not completely eliminated, as confirmed by tests carried out during increasing reaction times, under isothermal conditions (310 °C) in the presence of oxygen (figure not shown). After 5 h reaction time, glycerol conversion was only 13–14% lower than the initial value (decreasing from 90% to 76%, whereas in the absence of oxygen the conversion decline was much greater during a similar value of elapsed reaction time, see Fig. 5); conversion, however, dropped to 37% after 24 h reaction time. These data confirm the existence of a deactivation phenomenon even when oxygen was co-fed with glycerol.

Another important aspect is that the yield to CO<sub>x</sub> was relevant (even at 290 °C there was a non-negligible formation of CO<sub>2</sub>, Fig. 6), thus suggesting that the sulfate groups play a catalytic oxidizing role [21–25].

### 3.5. The reactivity of sulfated zirconia: the reaction network

Concerning the reaction mechanisms leading to acrolein and by-product formation, the following can be inferred from the literature [4]. The primary reaction products of glycerol dehydration are enol intermediates: they are very reactive and





**Fig. 6.** Effect of temperature on catalytic behaviour of sulfated zirconia catalyst in glycerol dehydration: comparison of anaerobic and aerobic conditions. Feed composition: glycerol/water/helium = 2/40/58 (molar ratios) (open symbols) or glycerol/oxygen/water/helium = 2/4/40/54 (molar ratios) (full symbols). Residence time 0.2 s; catalyst mass 0.1 g; linear velocity 0.15 m/min. Symbols: glycerol conversion (▲, △), selectivity to acrolein (◆, ◇), conversion of oxygen during aerobic tests (+), selectivity to heavy compounds (■, □) and CO + CO<sub>2</sub> (●, ○).

transform into either the stable hydroxyacetone (acetol), from 1,2-dihydroxypropene, or into 3-hydroxypropanal (via tautomerisation of 1,3-dihydroxypropene). 3-Hydroxypropanal, however, is only a hypothetical intermediate; in fact, it has never been isolated, possibly due to its high instability. The main by-products of the reaction are acetaldehyde, hydroxyacetone, propanal, allyl alcohol (formed by hydrogenation of acrolein), light alcohols (methanol, ethanol) and – in the presence of oxygen – also carbon oxides (that also are formed by the decarbonylation and decarboxylation of various molecules [15,37]), propionic acid, acrylic acid and acetic acid [6–16,34–39]. Other products reported are (i) 1,2-propandiol, possibly formed by the hydrogenation of acetol with *in situ* generated hydrogen [8,9,15], (ii) phenol [19,37], probably formed from a dimerisation–cyclisation reaction of glycerol followed by a subsequent dehydration, or from acrolein and acetone via a Diels–Alder reaction, and (iii) acetone [13,14,37], formed by hydroxyacetone hydrogenation and dehydration. It is suggested that acetaldehyde and methanol form formaldehyde and acetic acid, from the intermediate 3-hydroxypropanal [15,16,37]. Hydrogen is formed by the dehydrogenation of glycerol and various intermediates.

All the authors, however, report the formation of a certain number of unidentified oxygenated compounds and, in many cases, the C balance is lower than 100%, a clear indication of the formation of heavy, undetected compounds. Heavy compounds may form either by direct glycerol transformation (to give linear, cyclic and branched oligomers), or as consecutive transformations

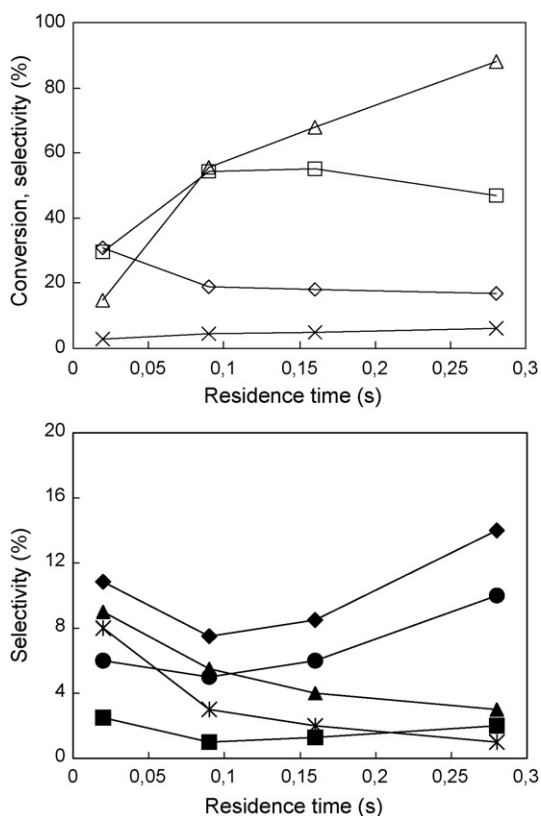
from both acrolein and acetol; these heavy compounds, which may also include oxygenated aromatics, are precursors for coke formation.

In order to gain information on the nature of the heavy compounds formed, we carried out the derivatisation of products obtained during aerobic tests, by means of reaction with methanol and BF<sub>3</sub> in alcoholic solution (after evaporation of water solvent), in order to obtain the corresponding volatile esters and ethers, which were then analyzed by means of GC–MS. This method allowed us to identify the methyl derivatives (esters and acetals) of C<sub>6</sub> unsaturated dicarboxylic acid (muconic acid), succinic acid, 1,1,2,2-ethantetrol, 2,2-dihydroxypropionic acid, and other lighter compounds. Acetals may derive from the reaction of carbonyl compounds with methanol during derivatisation. However, the presence of esters is surprising, suggesting that the formation of acids is favoured in an oxidizing environment even with sulfated zirconia; it cannot be excluded that acids are formed by the (oxidative) dehydrogenation of geminal glycols, the latter being formed by reaction of aldehydic carbonyl moieties with the large excess of water present in the reaction environment. The presence of C<sub>6</sub> compounds as prevailing heavy by-products also points out the important role of dimerization or (aldol) condensation reactions.

A role of basic sites in catalyzing the formation of heavy compounds cannot be ruled out; in fact, zirconia holds both basic and acid sites [40], and it forms heavy compounds with selectivity as high as 80–90% (Fig. 3). The same might occur with sulfated zirconia, especially when the amount of sulfate groups is lower than that required to achieve a complete “monolayer” coverage of the zirconia surface. In our case, the loading of 4.4 wt% sulfate corresponds to approximately 2.3 SO<sub>4</sub><sup>2–</sup>/nm<sup>2</sup>, that in turn corresponds to about the half-monolayer coverage [41]. However, we can exclude a contribution from basic sites because yield to heavy compounds obtained with zirconia at low temperature was much less than that achieved with the sulfated zirconia, due to the much lower glycerol conversion. This means that the greater fraction of heavy compounds forms because of the presence of the strong acid sites in sulfated zirconia. Moreover, it is reported in the literature that sulfation process causes the basicity of zirconia to be dramatically depressed, the most basic OH<sup>–</sup> and the coordinatively unsaturated O<sup>2–</sup> sites being completely consumed by the sulfation process [40,42].

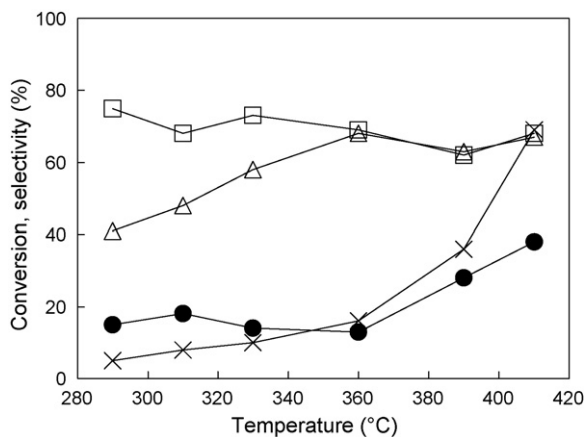
The low selectivity to acrolein achieved with our catalyst, as described in the present work, is due to both the formation of several C<sub>2</sub> and C<sub>3</sub> by-products, CO<sub>x</sub>, and heavy compounds. In order to obtain more precise information on the reaction network, we carried out experiments under isothermal conditions, by varying the residence time in the presence of oxygen. Each experiment was carried out with fresh sample, by changing the amount of catalyst loaded; for each experiment, the outlet feed composition was analyzed after 1 h from the start-up of the glycerol feed.

The increased residence time led to an increase in glycerol conversion (Fig. 7); oxygen conversion was less than 20% over the entire range of temperature examined, because of the very low formation of CO<sub>2</sub>. The selectivity to acrolein was low, at 31%, even at low glycerol conversion (15%). This was due to the formation of both light by-products (hydroxyacetone, acetone, acetaldehyde and others), and heavy by-products (selectivity around 25% at 15% glycerol conversion). However, the selectivity to heavy compounds increased when the conversion was increased; this is clear evidence of the fact that heavy compounds were formed both by direct reaction on glycerol and by consecutive reactions. The selectivity to acrolein, hydroxyacetone and other unknown compounds decreased, whereas that to CO<sub>x</sub> increased, once again because of the greater contribution of consecutive reactions. The latter were also evident from the results of the experiments reported in Fig. 8. An aqueous solution of acrolein (7 wt% acrolein in water) was vaporized and fed over the catalyst, in the presence of oxygen; in this case,

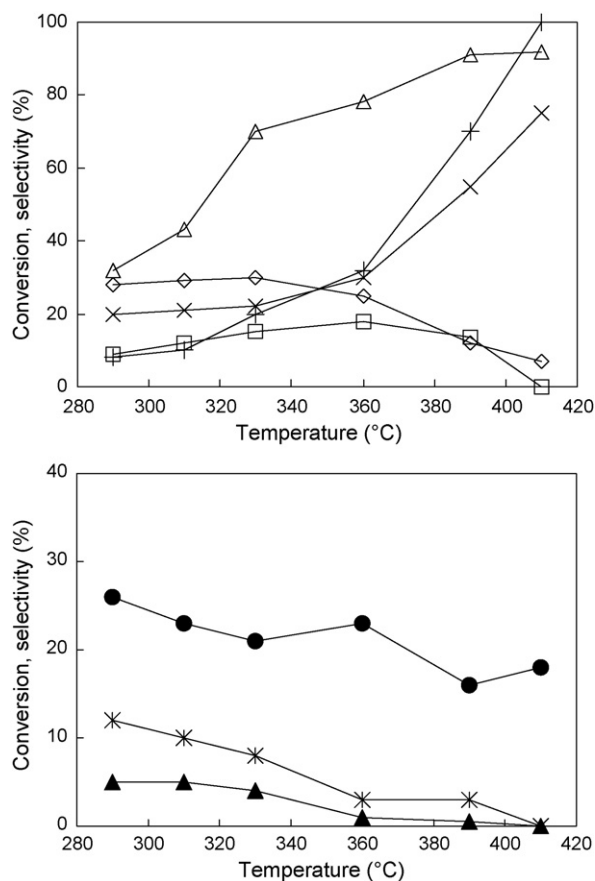


**Fig. 7.** Effect of residence time on catalytic behaviour of sulfated zirconia catalyst in glycerol dehydration. Feed composition: glycerol/water/oxygen/helium = 2/4/40/54 (molar ratios). Temperature 310 °C; catalyst mass was varied; linear velocity 0.15 m/min. Symbols: conversion of glycerol ( $\Delta$ ), selectivity to acrolein ( $\diamond$ ), heavy compounds ( $\square$ ), acetone ( $\blacklozenge$ ), acetaldehyde ( $\bullet$ ), propionaldehyde ( $\blacksquare$ ),  $\text{CO} + \text{CO}_2$  ( $\times$ ), hydroxyacetone ( $*$ ) and others (minor identified + unknown compounds) ( $\blacktriangle$ ).

the only products identified were acetaldehyde and carbon oxides, with also a significant formation of heavy compounds, especially at low temperatures. Therefore, acrolein is highly reactive with these catalysts, and when the conversion of glycerol is pushed, it is extensively converted to by-products.



**Fig. 8.** Effect of temperature on catalytic behaviour of sulfated zirconia in acrolein transformation. Feed composition: acrolein/oxygen/water/helium = 1/4/43/52 (molar ratios). Residence time 0.2 s; catalyst mass 0.1 g; linear velocity 0.15 m/min. Symbols: conversion of acrolein ( $\Delta$ ), selectivity to acetaldehyde ( $\bullet$ ), heavy compounds ( $\square$ ) and  $\text{CO} + \text{CO}_2$  ( $\times$ ).

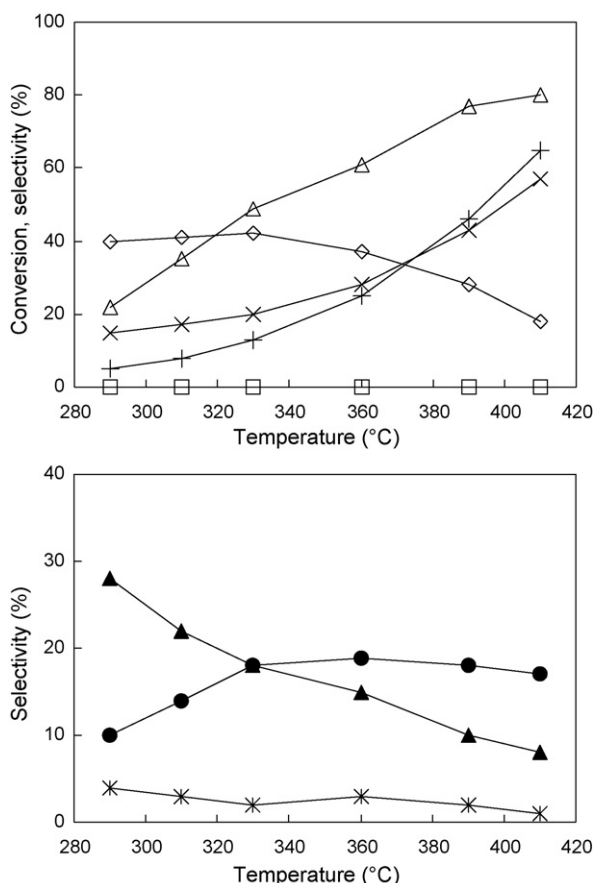


**Fig. 9.** Effect of temperature on the catalytic behaviour of sulfated zirconia in glycerol dehydration: tests at high linear velocity. Feed composition: glycerol/water/oxygen/helium = 2/4/40/54 (molar ratios). Residence time 0.2 s; catalyst mass 0.5 g; linear velocity 0.75 m/min. Symbols: conversion of glycerol ( $\Delta$ ), conversion of oxygen (+), selectivity to acrolein ( $\diamond$ ), heavy compounds ( $\square$ ),  $\text{CO} + \text{CO}_2$  ( $\times$ ), acetaldehyde ( $\bullet$ ), hydroxyacetone ( $*$ ) and others (minor identified + unknown compounds) ( $\blacktriangle$ ).

### 3.6. Searching for a better selectivity to acrolein: the role of mass-transfer limitation phenomena

The results of the experiments carried out in function of temperature (Fig. 6) highlight that mass-transfer phenomena can limit the reaction rate. These phenomena might eventually be responsible for the presence of undesired reactions leading to the formation of heavy compounds. In order to confirm this hypothesis, we carried out experiments keeping the same residence time (0.2 s), but using higher linear velocity, i.e. equal to 0.75 m/min (measured at 20 °C, and calculated considering the entire reactor section, as if it had no catalyst loaded within), that is five times greater than that used for the experiments shown in Figs. 3–7. It is worth noting that these experiments were carried out using a total GHSV of 18,000 h<sup>-1</sup> (360 h<sup>-1</sup> by glycerol): values that are higher than those typically reported in papers for this reaction [7,15]. The results of the test carried out at high linear velocity are shown in Fig. 9 (experiments were carried out in the presence of oxygen, to limit deactivation phenomena). The comparison with the results shown in Fig. 6 (full symbols), made at the same residence time but with lower linear velocity, enabled us to make the following observations:

1. At high linear velocity, the conversion of glycerol showed a marked increase in function of temperature, with apparent activation energy of  $29 \pm 2$  kcal/mol. The conversion at a low temperature was lower than that achieved for the same temper-



**Fig. 10.** Effect of temperature on the catalytic behaviour of sulfated zirconia in glycerol dehydration: tests at high linear velocity and low residence time. Feed composition: glycerol/water/oxygen/helium = 2/4/40/54 (molar ratios). Residence time 0.1 s; catalyst mass 0.25 g; linear velocity 0.75 m/min. Symbols: conversion of glycerol (Δ), conversion of oxygen (+), selectivity to acrolein (◇), heavy compounds (□), CO + CO<sub>2</sub> (×), acetaldehyde (●), hydroxyacetone (\*) and others (minor identified + unknown compounds) (▲).

ature and residence time, but using lower linear velocity; this difference is typically observed when inter-particle mass and heat transfer limitations cause higher local temperatures (for exothermal reactions) and hence higher conversion rates. Glycerol dehydration is slightly endothermal, but in the presence of oxygen the overall reaction becomes exothermal, because of the formation of carbon oxides.

- The selectivity to acrolein and CO<sub>x</sub> was higher than that achieved under conditions of mass-transfer limitation, whereas that to other by-products and heavy compounds was remarkably lower; acetone and propionaldehyde were absent. The selectivity to heavy compounds was lower at both low (compare with Fig. 7) and high conversion (compare with Fig. 6): a clear indication of the reduced contribution of both parallel and consecutive reactions on glycerol and acrolein, respectively. The preferred occurrence of a bimolecular reaction, leading to heavy by-products, is also a typical phenomenon encountered when the concentration of products is unusually high in the boundary layer surrounding the catalyst, because of the presence of mass-transfer limitations that hinder the counter-diffusion of products towards the bulk reactants phase.

It is worth noting that the lower formation of heavy compounds was also confirmed by means of the determination of the residual C amount on spent catalyst. The latter was equal to 2.35 wt%

after approximately 15 h reaction time under aerobic conditions, at 400 °C and high GHSV, whereas it was 8.5 wt% after tests carried out at low linear velocity (but same overall residence time and same reaction time).

The experiments shown in Fig. 9 confirm that one problem met with this reaction is the existence of inter-particle mass-transfer limitations, contributing to the low selectivity to acrolein. As shown by tests reported in Fig. 2, the sulfated zirconia catalyst can retain water up to almost 450 °C. It is likely that due to the highly hydrophilic surface of sulfated zirconia, a boundary layer made of condensed water (the main component of the reaction medium) forms, and that the thickness of this layer is a function of fluidynamic conditions in the reactor. We would like also to note that this problem has not been reported in earlier papers, and therefore seems to be peculiar of this catalyst and of its highly hydrophilic properties. The presence of strong Brønsted sites, also generated by interaction of water with strong Lewis sites, and reaction conditions that facilitate the development of the stagnant boundary layer (low linear velocity), both contribute to the formation of by-products and hence to the low selectivity to acrolein achieved with this catalytic system. Relatively high linear velocities used for experiments shown in Fig. 9 are necessary to push the system towards the development of non-laminar regimes, so to lower diffusion limitations and the contribution of reactions leading to the formation of condensation compounds.

Finally, Fig. 10 shows the effect of temperature when the same high linear velocity, but with a lower residence time (0.1 s instead of 0.2 s), is used, if compared to the experiments in Fig. 9. As expected, the conversion achieved was lower than that shown in Fig. 9, and the selectivity to acrolein was higher (42% at 49% glycerol conversion); in this case the major by-products were CO<sub>x</sub> (with a selectivity that was lower than that shown in Fig. 9, especially at high temperatures) and other light compounds but, remarkably, the formation of heavy compounds was practically nil over the entire range of temperatures examined. This means that the combination of a high linear velocity (that allows the minimisation of mass-transfer limitations) and a high GHSV value (that however has the drawback of a lower glycerol conversion) can kinetically limit both the parallel and consecutive transformations leading to heavy by-products formation, and achieve higher acrolein selectivity with the sulfated zirconia catalyst.

#### 4. Conclusions

The reactivity of sulfated zirconia in the gas-phase dehydration of glycerol into acrolein – a reaction aimed at the valorisation of glycerol surplus obtained in biodiesel production – was examined with the aim of finding the effect of various reaction parameters on catalytic behavior.

The conversion of glycerol suffered from an extensive deactivation phenomena, especially when the reaction was carried out without oxygen co-feeding. The selectivity to acrolein was limited by the concomitant formation of several by-products that formed by both parallel reaction upon glycerol and consecutive reaction upon acrolein. The principal by-products were heavy compounds, the selectivity of which was decreased and finally made nil through a careful control of the reaction conditions, especially of the linear velocity of the inlet gas-vapours stream. This fact, in addition to other experimental evidences, suggested that the formation of heavy compounds mainly occurs under mass-transfer limitation conditions. These findings provide information on the most important reaction parameters that affect the reactivity behaviour during the acid-catalysed dehydration of glycerol.

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